

# PATENT SPECIFICATION

NO DRAWINGS

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## COMPLETE SPECIFICATION

### Improvements in or relating to Lead-acid Accumulator Electrodes and Accumulators Containing such Electrodes

We AKTIEBOLAGET TUDOR, a Swedish Body Corporate, of Box 103, Stockholm 1, Sweden, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to lead-acid accumulators, and more particularly to improved electrodes for such accumulators, such improvements being obtained according to the invention by the composition of the alloy in the electrode-grid and, where applicable, other conductive parts within the accumulator cell.

The invention achieves improved lead-acid accumulator cells by an appreciably reduced self-discharge and the possibility of fully charging the battery at low tension.

The electrode grids of the type used in lead-acid accumulators are generally formed by lead-antimony alloys containing from 4 to 11% of antimony and smaller quantities of other metals, such as arsenic, silver, tin, copper, etc. During charging and discharge the material of the positive electrodes is subjected to electrochemical attack as a result of which, *inter alia*, some of the antimony dissolves. Antimony may also dissolve from the negative grids during discharge. The antimony is deposited at the negative electrodes, more particularly during charging, in a very active metallic form on the negative substance. A local cell effect thus forms between the precipitated antimony and the electrode material at the negative electrodes. This local cell action, which may also occur on other conductive parts belonging to the negative electrodes or electrode groups, partly causes

self-discharge and hence evolution of hydrogen and partly reduces the charging voltage. Where a negative plate containing pure lead is charged, the decomposition voltage, that is, the voltage at which hydrogen is evolved, is so high that the battery can be fully charged before such hydrogen begins to evolve. If there are traces of antimony on the negative plate, the hydrogen precipitation potential drops at the negative electrode and hydrogen evolution begins long before the plate is fully charged. If the antimony precipitation is large enough, the negative plate cannot be fully charged, irrespective of the charging power, because all the current is used in precipitating hydrogen.

The above disadvantages can be obviated by the use of pure soft lead in the electrodes. However, the mechanical strength and life of the battery are adversely affected because of the poor mechanical properties of the lead.

Attempts have previously been made to combine the good mechanical properties of antimony lead with the good electrochemical properties of soft lead by coating antimony lead parts with soft lead, usually by any electroplating process. The attempt has also been made to overcome the difficulties by giving the electrode grids a finer grain structure. Certain physical treatment steps are required for this purpose, for example, shock cooling of the electrode grids immediately after casting or a rolling or pressing process. None of the methods tried has proved suitable and have therefore been abandoned. There are numerous reasons for this, for example, costs, and the required refinement of the grain structure did not come up to expectations as regards resistance to corrosion,

One of the objects of the invention is to provide accumulator cells which can be charged and discharged with practically negligible gas evolution. Another object is to provide an accumulator cell with insignificant or no self-discharge.

According to the invention there is provided a lead-acid accumulator electrode of the type containing load-bearing and conductive grid rods of active material surrounding the same, characterised in that the grid rods are composed of a lead alloy consisting of lead, tellurium, silver and arsenic, the combined content of tellurium, silver and arsenic being not more than 0.1% of the weight of the alloy with the remainder being pure lead.

The combined quantity of alloying additives is preferably 0.05% of the weight of the alloy.

Over the course of years many lead alloys have been disclosed which have often been an improvement as compared with pure lead antimony alloys. However, it has not been possible to prevent the self-discharge effect as a result of the formation of local elements and it was not possible to increase the decomposition voltage and hence the charging voltage sufficiently to enable charging to be carried out without gas evolution. The small quantities of alloying additives used according to the invention have proved to give a lead alloy which, apart from its high electrochemical resistance has sufficiently high mechanical strength for the purpose in view. As far as mechanical strength is concerned, this was unexpected in view of the absence of antimony and must be regarded as quite surprising.

The small proportion of alloying additives means that there is very little risk of the additives migrating in such a quantity as to reduce the decomposition voltage for the electrolyte.

Of course nearly all metals have a lower precipitation potential for hydrogen than pure lead so that the purity of the lead determines the maximum permissible charging voltage without gas evolution. This in turn means that the invention has made it possible completely to charge an accumulator cell without any risk of reaching the decomposition voltage. The accumulator cell according to the invention is advantageously charged to 2.4 volts, below which limit there is practically no gas evolution.

As regards mechanical strength, tests have shown that an alloy consisting of a trace of arsenic, 0.07% of tellurium and 0.007% of silver has a creep strength of  $35.6 \cdot 10^{-4}$  mm/min. under a load of 0.71 kg per sq. mm as against soft lead where the value is  $156.0 \cdot 10^{-4}$  mm/min.

A list of test results is given below with respect to elongation under various loads for three different material compositions:

The first table relates to soft lead, the second to an alloy containing 11.27% of antimony, and the third to an alloy according to the invention with the above composition.

Table I

| Soft lead               |       |                 |         |
|-------------------------|-------|-----------------|---------|
| 0.71 kg/mm <sup>2</sup> | 156.0 | $\cdot 10^{-4}$ | mm/min. |
| 0.57 "                  | 25.6  | $\cdot 10^{-4}$ | "       |
| 0.50 "                  | 6.25  | $\cdot 10^{-4}$ | "       |
| 0.35 "                  | 0.96  | $\cdot 10^{-4}$ | "       |

Table II

| 11.27% of antimony      |      |                 |        |
|-------------------------|------|-----------------|--------|
| 0.71 kg/mm <sup>2</sup> | 3.52 | $\cdot 10^{-4}$ | mm/min |
| 0.57 "                  | 2.44 | $\cdot 10^{-4}$ | "      |
| 0.50 "                  | 2.06 | $\cdot 10^{-4}$ | "      |
| 0.35 "                  | 0.98 | $\cdot 10^{-4}$ | "      |

Table III

| 0.71 kg/mm <sup>2</sup> | 35.6 | $\cdot 10^{-4}$ | mm/min |
|-------------------------|------|-----------------|--------|
| 0.57 "                  | 5.27 | $\cdot 10^{-4}$ | "      |
| 0.50 "                  | 3.33 | $\cdot 10^{-4}$ | "      |
| 0.35 "                  | 0.8  | $\cdot 10^{-4}$ | "      |

From the table it is apparent that an antimony-free lead alloy with good strength properties can be obtained provided that the alloying additives are kept within the initially indicated values. The antimony alloy in the test series has much better values, particularly under higher loading, in respect of tensile strength, which is not necessary incidentally, with reference to loads occurring in this context.

Very high tensile loads will occur on the electrode grids only with very long electrodes, such as are found, for example, in submarine batteries. In such electrodes, however, the grids are relieved by external electrode casings or other support means provided in the accumulator cell.

Of course the load due to the dead-weight of grid bars in a submarine accumulator electrode is only about 0.005 kg/mm<sup>2</sup> and the very much higher tensile loading actually occurring and resulting in elongation of the positive plates must have other causes. Experience has shown that a soft lead electrode grid has a much greater elongation than can be caused by the dead-weight. It may be assumed that the reason for the phenomenon is to be found in stresses in the lead peroxide layer forming on the grid bars, and this results in loads of the order of 0.4 kg/mm<sup>2</sup>. The test results show that with the loads which can occur in this context the alloy according to the invention is much superior to soft lead although not equally resistant to tensile stresses as antimony alloys it is sufficiently strong for the purposes in question.

A lead alloy containing 0.065% tellurium, 0.008% of silver and 0.009% of arsenic, remainder lead, has approximately the same

strength properties and very good resistance to corrosion.

WHAT WE CLAIM IS:—

1. A lead-acid accumulator electrode of the type containing load-bearing and conductive grid rods of active material surrounding the same, characterised in that the grid rods are composed of a lead alloy consisting of lead, tellurium, silver and arsenic, the combined content of tellurium, silver and arsenic being not more than 0.1% of the weight of the alloy with the remainder being pure lead.
2. A lead-acid accumulator electrode as claimed in claim 1, substantially as hereinbefore described.
3. A lead-acid accumulator having an electrode as claimed in claim 1 or claim 2.

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